

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification:

C09D 167/02, C08G 18/42, C09D 175/06 A1

(11) International Publication Number:

WO 95/01407

(43) International Publication Date:

12 January 1995 (12.01.95)

(21) International Application Number:

PCT/US94/06564

(81) Designated States: CA, JP, KR, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

(22) International Filing Date:

13 June 1994 (13.06.94)

(30) Priority Data:

084,103

1 July 1993 (01.07.93)

US

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(71) Applicant: EASTMAN CHEMICAL COMPANY [US/US];
100 North Eastman Road, Kingsport, TN 37660 (US).

(72) Inventors: BARBEE, Robert, B.; 201 Mahlon Drive,
Kingsport, TN 37663 (US). CHANG, Yeong-Ho; 1020
Norfolk Place, Kingsport, TN 37660 (US).

(74) Agent: GRAVES, Bernard, J., Jr.; P.O. Box 511, Kingsport,
TN 37662-5075 (US).

(54) Title: POWDER COATING COMPOSITIONS

(57) Abstract

Provided are thermosetting powder coating compositions which upon application to a substrate and curing provide coatings having superior weathering, impact, and flexibility properties. The compositions are a blend of an amorphous resin having cycloaliphatic diol residues, a semicrystalline resin, and a crosslinker. The binder portion of the composition may be either hydroxyl or carboxyl functional or a mixture thereof. Also provided are shaped or formed articles coated with the cured compositions.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

POWDER COATING COMPOSITIONS

This invention belongs to the field of powder coatings. More particularly, this invention relates to thermosetting powder coating compositions.

Plastic materials used in the manufacture of powder coatings are classified broadly as either thermosetting or thermoplastic. In the application of thermoplastic powder coatings, heat is applied to the coating on the substrate to melt the particles of the powder coating and thereby permit the particles to flow together and form a smooth coating.

Thermosetting coatings, when compared to coatings derived from thermoplastic compositions, generally are tougher, more resistant to solvents and detergents, have better adhesion to metal substrates and do not soften when exposed to elevated temperatures. However, the curing of thermosetting coatings has created problems in obtaining coatings which have, in addition to the above-stated desirable characteristics, good smoothness and flexibility. Coatings prepared from thermosetting powder compositions, upon the application of heat, may cure or set prior to forming a smooth coating, thereby resulting in a relatively rough finish referred to as an "orange peel" surface. Such a coating surface or finish lacks the gloss and luster of coatings typically obtained from thermoplastic compositions. The "orange peel" surface problem has caused many to apply thermosetting coatings compositions from organic solvent systems which are inherently undesirable because of the environmental and safety problems that may be occasioned by the evaporation of the solvent system. Solvent-based coating compositions also suffer from the disadvantage of relatively poor percent utilization; i.e., in some modes of application, only 60 percent or less of the

- 2 -

solvent-based coating composition being applied contacts the article or substrate being coated. Thus, a substantial portion of solvent-based coatings can be wasted since that portion which does not contact the article or substrate being coated obviously cannot be easily reclaimed.

In addition to exhibiting good gloss, impact strength and resistance to solvents and chemicals, coatings derived from thermosetting coating compositions must possess good to excellent flexibility. For example, good flexibility is essential for powder coating compositions used to coat sheet (coil) steel which is destined to be formed or shaped into articles used in the manufacture of various household appliances and automobiles wherein the sheet metal is flexed or bent at various angles.

All aliphatic polyesters such as those derived from 1,4-, 1,3- and 1,2-cyclohexanedicarboxylic acid (CHDA) with 2,2,4,4-tetramethyl-1,3-cyclobutanediol or those from CHDA and hydrogenated bisphenol A have excellent weatherability. These resins can be made with T_g (glass transition temperature) suitable for powder coatings. Coatings from these resins, however, generally suffer from poor flexibility and poor impact strength.

25 Powder coatings based on acrylic resins are known to have excellent weathering performance but are generally more expensive and impact strength and flexibility are relatively poor.

British Patent 962,913 discloses polyesters
30 containing CHDA and 2,2,4,4-tetramethyl-1,3-cyclo-
butanediol useful as film and molding plastics.

U. S. Patent No. 3,313,777 describes polyesters containing CHDA and 2,2,4,4-tetramethyl-1,3-cyclobutanediol useful as film and molding plastics.

35 U. S. Patent 4,363,908 discloses copolyesters

- 3 -

containing CHDA and 2,2,4,4-tetramethyl-1,3-cyclobutanediol useful as adhesives.

U. S. Patent 4,525,504 discloses stabilized polyesters with improved weatherability based on CHDA and 2,2,4,4-tetramethyl-1,3-cyclobutanediol. These polyesters are high molecular weight polyesters useful in molding plastics.

U. S. Patent 4,910,292 discloses water-dissipatable polyesters useful in coatings. 2,2,4,4-Tetramethyl-1,3-cyclobutanediol is listed as a possible glycol component.

U. S. Patent 5,097,006 and Research Disclosure, May 1990, Number 313, Publication No. 31336 describe an aliphatic polyester derived from 1,4-CHDA and a glycol component comprised of cycloaliphatic diols; the compositions are described as having improved weatherability.

This invention provides to thermosetting powder coatings based on a blend of an amorphous aliphatic resin and a low Tg, aliphatic, semi-crystalline (SC) resin. The SC resin significantly improves impact strength while maintaining the excellent QUV weathering properties of the aliphatic resins.

The amorphous resins are comprised of cyclohexanedicarboxylic acid (CHDA) and cycloaliphatic diols such as 2,2,4,4-tetramethyl-1,3-cyclobutanediol, 1,4-cyclohexanediol, or hydrogenated bisphenol A. The amorphous resins preferably have a glass transition temperature (Tg) of 50° to 70°C and a hydroxyl or acid number of 30 to about 80.

The SC aliphatic resins preferably have good crystallinity and low Tg, such as one based on trans-1,4-cyclohexanedicarboxylic acid and 1,4-butanediol. Preferred SC resins have a Tm of 60-160°C and a hydroxyl or acid number of about 25-65.

- 4 -

It should be appreciated that in the compositions of the present invention, when component (a) is hydroxyl-functional, component (b) is preferably also hydroxyl-functional; in such a case, conventional crosslinkers are utilized. Conversely, when component (a) is carboxyl-functional, component (b) is also preferably carboxyl-functional; in such a case, conventional crosslinkers for acid-functional systems will be utilized. It is also within the scope of the present invention that the binder portion of the composition, i.e., components (a) and (b), may also be comprised of a mixture of hydroxyl and carboxyl functional; in other words, (a) may be hydroxyl-functional and (b) may be carboxyl-functional, and vice-versa. In such a case, the crosslinker will necessarily be a blend of suitable crosslinkers appropriate to the amounts of hydroxyl and carboxyl functionality present in the system. As used herein, the terms "hydroxyl-functional" and "carboxyl-functional" as used to describe the blend of (a) and (b) or the composition, is used in its ordinary art-recognized meaning. In other words, such terms denote whether the resin (or binder) is predominantly carboxyl- or hydroxyl- functional in character, thereby dictating the choice of crosslinker. In such a case, for example, a hydroxyl functional resin will have an acid number of less than about 15 and a carboxyl functional resin will have a hydroxyl number of less than about 15. The coating composition may be based on hydroxyl resins and crosslinkers such as blocked polyisocyanate, tetramethoxymethyl glycoluril or melamine derivatives. Alternatively, the composition may be comprised of a carboxyl resin and a crosslinker such as triglycidylisocyanurate (TGIC) or an activated β -hydroxylalkyl amide such as Bis(N,N-dihydroxy-ethyl)adipamide. Optionally, additives such as benzoin,

- 5 -

flow aids, pigments and catalyst may be used. Coatings provided by this invention maintain superior resistance to QUV with improved impact and flexibility.

The present invention provides a thermosetting
5 coating composition comprising

- 10 (a) an amorphous polyester comprised of residues of cyclohexanedicarboxylic acid and a cycloaliphatic diol, said amorphous polyester having a glass transition temperature (T_g) of about 50°C to 70°C and a hydroxyl or an acid number of about 30 to 80;
- 15 (b) a semicrystalline polyester comprised of residues of cyclohexanedicarboxylic acid and a linear diol, said linear diol having 4, 6, 8, or 10 carbon atoms, said semicrystalline polyester having a T_m of about 60°-160°C and a hydroxyl or an acid number of about 30 to 80;
20 and
- (c) a cross-linking effective amount of a cross-linking agent.

25 As a further aspect of the present invention, there is provided a thermosetting coating composition comprising

- 30 (a) an amorphous polyester comprised of residues of cyclohexanedicarboxylic acid and a cycloaliphatic diol, said amorphous polyester having a glass transition temperature (T_g) of about 50°C to 70°C and a hydroxyl or an acid number of about 30 to 80;

35

- 6 -

(b) a semicrystalline polyester comprised of residues of cyclohexanedicarboxylic acid and a linear diol, said linear diol having 4, 6, 8 or 10 carbon atoms, said semicrystalline polyester having a T_m of about 60–160°C and a hydroxyl or an acid number of about 30–80; provided that when (a) has an acid number of 30 to 80, (b) has an acid number of 30 to 80, and when (a) has a hydroxyl number of 30 to 80, (b) has a hydroxyl number of 30 to 80; and

(c) a cross-linking effective amount of a cross-linking agent.

The powder coating compositions provided by the present invention are useful in coating articles, particularly metal articles, and upon curing provide coatings possessing an excellent balance of weatherability and impact strength. The amorphous resins of the above composition are preferably comprised of 1,4-, 1,3- and 1,2-cyclohexanedicarboxylic acid (CHDA) and 2,2,4,4-tetramethyl-1,3-cyclobutanediol; CHDA and hydrogenated bisphenol A; or CHDA and 1,4-cyclohexanediol. The resin may be modified with other diacids or diols but must have T_g suitable for powder coating compositions. The amorphous polyester resin preferably has a number average molecular weight (M_n) of from about 1,500 to about 10,000, most preferably from about 2,000 to 6,000 and a glass transition temperature (T_g) of preferably about 45°C to 100°C, most preferably 50 to 70°C and hydroxyl or acid number of from about 20 to 100, preferably from about 30 to about 80, for cross-linking.

The semi-crystalline resins of the compositions of the present invention are preferably all aliphatic

- 7 -

resins which exhibit high crystallinity and low Tg. As an especially preferred aspect of the present invention, the semi-crystalline resin is one comprised of trans-1,4-cyclohexanedicarboxylic acid and 1,4-butanediol with optional slight modification with trimethylolpropane, i.e., from about 0 weight percent to 12 weight percent, based on the weight of the diol component. The preferred aliphatic poly(tetramethylene-trans-1,4-cyclohexanedicarboxylate) polyester of this invention has a Tm of about 110-160°C and a hydroxyl or acid number in the range of about 25-65 and an inherent viscosity of about 0.1 to 0.4. The semicrystalline resin may also contain trimethylolpropane as branching agent to adjust the crosslinking density as desired depending on the crosslinker used.

The linear diol in component (b) herein denotes a diol selected from the group consisting of 1,4-butanediol; 1, 6-hexanediol; 1, 8-octanediol; and 1, 10-decanediol. Preferably, the linear diol is 1,4-butanediol or 1,6-hexanediol.

The relative amount of amorphous to crystalline resin can be varied depending on factors such as each of the resin's properties, the crosslinker employed, the degree of pigment loading and the final coating properties desired. Preferably, the amorphous resin component will range from about 20 to about 80 weight percent based on the total weight percent of components (a) and (b), and the semicrystalline resin will range from about 80 to about 20 weight percent based on the total weight percent of components (a) and (b). Most preferably, components (a) and (b) will be present in about a 1:1 (weight:weight) ratio.

Powder coating compositions of this invention may be of course utilize different crosslinking chemistries depending on the characteristics of components (a) and

- 8 -

(b), i.e., whether the resin is predominantly hydroxyl or the acid functional.

Examples of powder coating compositions from hydroxyl resins are: (1) a polyurethane system made from a hydroxyl functional resin and a polyisocyanate, (2) a glycoluril system from a hydroxyl functional resin and a glycoluril crosslinker such as tetramethoxymethyl glycoluril or (3) a melamine system from a hydroxyl functional resin and a melamine designed for powder coating application. An example of a polyurethane powder coating of this invention is comprised of:

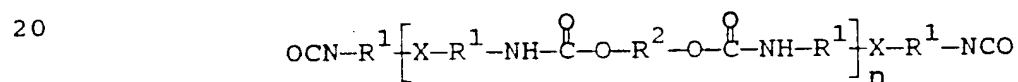
- (a) a blend of hydroxyl amorphous/semi-crystalline polyesters described herein
- (b) a blocked polyisocyanate crosslinker and,
- (c) optionally, additives such as benzoin, flow aids, pigments and catalyst.

The most readily-available, and thus the preferred, blocked isocyanate cross-linking agents or compounds are those commonly referred to as ϵ -caprolactam-blocked isophorone diisocyanate, e.g., those described in U.S. Patent Nos. 3,822,240, 4,150,211 and 4,212,962, incorporated herein by reference. However, the products marketed as ϵ -caprolactam-blocked isophorone diisocyanate may consist primarily of the blocked, difunctional, monomeric isophorone diisocyanate, i.e., a mixture of the cis and trans isomers of 3-isocyanato-methyl-3,5,5-trimethylcyclohexylisocyanate, the blocked, difunctional dimer thereof, the blocked, trifunctional trimer thereof or a mixture of the monomeric, dimeric and/or trimeric forms. For example, the blocked polyisocyanate compound used as the cross-linking agent may

- 9 -

be a mixture consisting primarily of the ϵ -caprolactam-blocked, difunctional, monomeric isophorone diisocyanate and the ϵ -caprolactam-blocked, trifunctional trimer of isophorone diisocyanate. The description herein of the cross-linking agents as "blocked isocyanates" refers to compounds which contain at least two isocyanato groups which are blocked with, i.e., reacted with, another compound, e.g., ϵ -caprolactam. The reaction of the isocyanato groups with the blocking compound is reversible at elevated temperatures, e.g., normally about 150°C, and above, at which temperature the isocyanato groups are available to react with the hydroxyl groups present on the free hydroxy groups of the polyester to form urethane linkages.

Alternatively, the blocked isocyanate may be a cross-linking effective amount of an adduct of the 1,3-diazetidione-2,4-dione dimer of isophorone diisocyanate and a diol having the structure



25

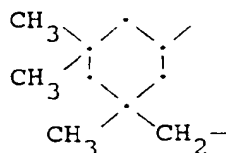
wherein

R^1 is a divalent 1-methylene-1,3,3-trimethyl-5-cyclohexyl radical, i.e., a radical having the structure

35

40

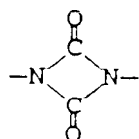
45



R^2 is a divalent aliphatic, cycloaliphatic, araliphatic or aromatic residue of a diol; and

- 10 -

X is a 1,3-diazetidine-2,4-dionediyl radical, i.e., a radical having the structure



wherein the ratio of NCO to OH groups in the formation of the adduct is about 1:0.5 to 1:0.9, the mole ratio of diazetidinedione to diol is from 2:1 to 6:5, the content of free isocyanate groups in the adduct is not greater than 8 weight percent and the adduct has a molecular weight of about 500 to 4000 and a melting point of about 70 to 130°C.

The adducts of the 1,3-diazetidine-2,4-dione dimer of isophorone diisocyanate and a diol are prepared according to the procedures described in U.S. Patent No. 4,413,079, incorporated herein by reference, by reacting the diazetidine dimer of isophorone diisocyanate, preferably free of isocyanurate trimers of isophorone diisocyanate, with diols in a ratio of reactants which gives as isocyanato:hydroxyl ratio of about 1:0.5 to 1:0.9, preferably 1:0.6 to 1:0.8. The adduct preferably has a molecular weight of 1450 to 2800 and a melting point of about 85 to 120°C. The preferred diol reactant is 1,4-butanediol. Such an adduct is commercially available under the name Hüls BF1540.

The amount of the blocked isocyanate cross-linking compound (or other crosslinker) present in the compositions of this invention can be varied depending on several factors such as those mentioned hereinabove relative to the amount of components (a) and (b) which are utilized. Typically, the amount of cross-linking

- 11 -

compound which will effectively cross-link the polymers to produce coatings having a good combination of properties is in the range of about 5 to 30 weight percent, preferably 15 to 25 weight percent, based on the total weight of components (a) and (b).

An example of a glycoluril powder coating composition of this invention is one comprised of:

- 10 (a) a blend of hydroxyl functional amorphous/semi-crystalline polyester resin described above;
- (b) a crosslinking agent from the glycoluril family of "aminoplast" crosslinking agents, such as tetramethoxymethyl glycoluril
15 commercially available as POWDERLINK 1174 from American Cyanamid; and
- (c) optionally a catalyst such as toluenesulfonic acid or methyltolyl sulfonimide.

20

Examples of powder coating compositions prepared from carboxyl functional resins are; (1) a weatherable epoxy system such as a TGIC (triglycidylisocyanurate) system and (2) the activated β -hydroxylalkyl amide-based system. An example of an epoxy system is:

25

- (a) a carboxyl functional amorphous/ semi-crystalline polyester blend described above, and as crosslinker,
- 30 (b) a weatherable epoxy such as triglycidylisocyanurate (TGIC) commercially available as ARALDITE PT-810 sold by Ciba Geigy, or alternatively, an acrylic resin containing pendant reactive epoxy functional groups, such

35

- 12 -

as the glycidyl group, e.g., glycidyl methacrylate polymer available from S.C. Johnson as PD 7610.

5 An example of an activated β -hydroxylalkyl amide system is:

- 10 (a) a carboxyl functional amorphous/ semi-crystalline polyester blend described above,
- (b) an activated β -hydroxylalkyl amide such as Bis(N,N-dihydroxyethyl)adipamide commercially available from Rohm and Haas as PRIMID XL552.

15 In the activated β -hydroxylalkyl amide system above, it is further preferred that a catalyst comprised of a carboxylate salt of a metal such as zinc, aluminum, or titanium, or an oxide of aluminum or zinc is present. Especially preferred as a catalyst is zinc stearate.

20 Further description of catalyst systems for an activated β -hydroxylalkyl amide system can be found in U.S. Application Seral No. 08/084,104, filed on this date, incorporated herein by reference.

25 As noted above, components (a) and (b) may be a mixture of carboxyl and hydroxyl functional resins. Thus, in a further preferred embodiment of the present invention, there is provided a thermosetting coating composition comprising a blend comprising

- 30 (a) an amorphous polyester comprised of residues of cyclohexanedicarboxylic acid and a cycloaliphatic diol, said amorphous polyester having a glass transition temperature (T_g) of about 50°C to 70°C and a hydroxyl or an acid
- 35 number of about 30 to 80;

SUBSTITUTE SHEET (RULE 26)

- 13 -

(b) a semicrystalline polyester comprised of residues of cyclohexanedicarboxylic acid and a linear diol, said linear diol having 4, 6, 8, or 10 carbon atoms, said semicrystalline polyester having a T_m of about 60°–160°C and a hydroxyl or an acid number of about 30 to 80; provided that when (a) has an acid number of 30 to 80, (b) has an acid number of 30 to 80, and when (a) has a hydroxyl number of 30 to 80, (b) has a hydroxyl number of 30 to 80; and

(c) a cross-linking effective amount of a cross-linking agent.

The 1,4-CHDA used for the preparation of the resin which is labeled "CA" in the experimental section below has a cis/trans ratio of about 60/40. Dimethyl trans-1,4-cyclohexanedicarboxylate, which has a trans isomer of at least 70% is used for the preparation of the resins labeled "CC" and "HC" in the experimental section.

The powder coating compositions of this invention may be prepared from the compositions described herein by dry-mixing and then melt-blending components (a) and (b) and the cross-linking compound, optionally a cross-linking catalyst, along with other additives commonly used in powder coatings, and then grinding the solidified blend to a particle size, e.g., an average particle size in the range of about 10 to 300 microns, suitable for producing powder coatings. For example, the ingredients of the powder coating composition may be dry blended and then melt blended in a Brabender extruder at 90° to 130°C, granulated and finally ground. The melt blending should be carried out at a temperature sufficiently low to prevent the unblocking of the

- 14 -

polyisocyanate cross-linking compound and thus avoiding premature cross-linking.

The powder coating compositions preferably contain a flow aid, also referred to as flow control or leveling agents, to enhance the surface appearance of cured coatings of the powder coating compositions. Such flow aids typically comprise acrylic polymers and are available from several suppliers, e.g., Modaflow from Monsanto Company and Acronal from BASF. Other flow control agents which may be used include Modarez MFP available from Synthron, EX 486 available from Troy Chemical, BYK 360P available from BYK Mallinkrodt and Perenol F-30-P available from Henkel. An example of one specific flow aid is an acrylic polymer having a molecular weight of about 17,000 and containing 60 mole percent 2-ethylhexyl methacrylate residues and about 40 mole percent ethyl acrylate residues. The amount of flow aid present may preferably be in the range of about 0.5 to 4.0 weight percent, based on the total weight of the resin component, and the cross-linking agent.

The powder coating compositions may be deposited on various metallic and non-metallic (e.g., thermoplastic or thermoset composite) substrates by known techniques for powder deposition such as by means of a powder gun, by electrostatic deposition or by deposition from a fluidized bed. In fluidized bed sintering, a preheated article is immersed into a suspension of the powder coating in air. The particle size of the powder coating composition normally is in the range of 60 to 300 microns. The powder is maintained in suspension by passing air through a porous bottom of the fluidized bed chamber. The articles to be coated are preheated to about 250° to 400°F (about 121° to 205°C) and then brought into contact with the fluidized bed of the powder coating composition. The contact time depends on

- 15 -

the thickness of the coating that is to be produced and typically is from 1 to 12 seconds. The temperature of the substrate being coated causes the powder to flow and thus fuse together to form a smooth, uniform,
5 continuous, uncratered coating. The temperature of the preheated article also effects cross-linking of the coating composition and results in the formation of a tough coating having a good combination of properties. Coatings having a thickness between 200 and 500 microns
10 may be produced by this method.

The compositions also may be applied using an electrostatic process wherein a powder coating composition having a particle size of less than 100 microns, preferably about 15 to 50 microns, is blown by means of
15 compressed air into an applicator in which it is charged with a voltage of 30 to 100 kV by high-voltage direct current. The charged particles then are sprayed onto the grounded article to be coated to which the particles adhere due to the electrical charge thereof. The coated
20 article is heated to melt and cure the powder particles. Coatings of 40 to 120 microns thickness may be obtained.

Another method of applying the powder coating compositions is the electrostatic fluidized bed process which is a combination of the two methods described
25 above. For example, annular or partially annular electrodes are mounted in the air feed to a fluidized bed so as to produce an electrostatic charge such as 50 to 100 kV. The article to be coated, either heated, e.g., 250° to 400°F, or cold, is exposed briefly to the
30 fluidized powder. The coated article then can be heated to effect cross-linking if the article was not preheated to a temperature sufficiently high to cure the coating upon contact of the coating particles with the article.

The powder coating compositions of this invention
35 may be used to coat articles of various shapes and sizes

- 16 -

constructed of heat-resistance materials such as glass, ceramic and various metal materials. The compositions are especially useful for producing coatings on articles constructed of metals and metal alloys, particularly steel articles. As noted above, since the compositions provided by the present invention cure at temperatures as low as 115°C, it is also possible to coat many thermoplastic and thermosetting resin compositions with the compositions of the present invention.

Further examples of formulation methods, additives, and methods of powder coating application may be found in User's Guide to Powder Coating, 2nd Ed., Emery Miller, editor, Society of Manufacturing Engineers, Dearborn, (1987).

The compositions and coatings of this invention are further illustrated by the following examples.

Experimental Section

The inherent viscosity (I.V.), in dl/g were determined in phenol/tetrachloroethane (60/40 w/w) at a concentration of 0.5g/100 ml.

The resin melt viscosity, in poise, were determined using an ICI melt viscometer at 200°C.

The acid number and hydroxyl number were determined by titration and reported as mg of KOH consumed for each gram of resin.

The glass transition temperature (Tg), was determined by differential scanning calorimetry (DSC) on the second heating cycle scanning at 20°C/minute after the sample has been heated to melt and quenched to below the resin Tg. Tg values are reported as midpoint.

The weight average molecular weight (Mw) and number average molecular weight (Mn) are determined by gel permeation chromatography in tetrahydrofuran (THF) using

- 17 -

polystyrene standard and a UV detector.

Impact strengths are determined using a Gardner Laboratory, Inc., impact tester per ASTM D 2794-84.

Pencil hardness is determined using ASTM D 3363-74.

- 5 The hardness is reported as the hardest pencil which will not cut into the coating. The results are expressed according to the following scale:
(softest) 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, 6H
(hardest).

- 10 The conical mandrel is performed using a Gardener Laboratory Inc., conical mandrel of specified size according to ASTM-522.

- The 20 and 60 degree gloss are measured using a gloss meter (Gardener Laboratory, Inc. Model GC-9095)
15 according to ASTM D-523.

- The QUV resistance is measured by the loss of gloss. QUV is run by alternately exposing the coated panel at 70°C to a 313 nm fluorescent tube for 8 hours followed by a condensation at 45°C for 4 hours. Gloss
20 is monitored every 100 hours of exposure. The number of hours needed to reduce the 60° gloss to 50% of the original is reported.

Carboxyl Resins

25

Carboxyl Resin CA

- To a 1000 ml, 3-neck round bottom flask were added 2,2,4,4-tetramethyl-1,3-cyclobutanediol (204.5 g, 1.418
30 moles), 2,2-dimethyl-1,3-propanediol (66.1 g, 0.635 moles), trimethylolpropane (8.5 g, 0.063 moles) and Fascat 4100 (0.6 g). The contents were heated to melt at 180°C and 1,4-cyclohexanedicarboxylic acid (328.2 g, 1.908 moles) is added. The flask was swept with 1.0
35 scfh nitrogen while the temperatures was raised from

- 18 -

180°C to 230°C over a 6-hour period. The batch temperature was maintained at 230°C for 8 hours. The resulting resin has an acid number of 3 mg KOH/g and an ICI melt viscosity of 15 poise at 200°C. 1,4-Cyclo-
5 hexanedicarboxylic acid (70.0 g) is added at 230°C and the melt was agitated at 230°C for 4 hours. The molten resin was poured to a syrup can where it cooled to a solid with the following properties:

10	I.V.	0.237 dl/g
	ICI Melt Viscosity at 200°C	52 poise
	Acid Number	37
	Hydroxyl Number	3
	DSC (2nd cycle)	
15	Tg	58°C
	Gel permeation chromatography	
	Mw	11,047
	Mn	3,308

20 Carboxyl Resin CB

To a 3000 ml, 3-neck round bottom flask were added hydrogenated bisphenol A (726.5 g, 3.027 moles), 2,2-dimethyl-1,3-propanediol (326.4 g, 2.847 moles) and
25 trimethylolpropane (24.3 g, 0.183 moles) and FASCAT 4100 (1.8 g). The contents were heated to melt at 180°C. 1,4-cyclohexanedicarboxylic acid (951.7 g, 5.526 moles) was added. The flask was swept with 1.0 scfh nitrogen while the temperatures was raised from 180°C to 230°C
30 over a 6-hour period. The batch temperature was maintained at 230°C for 8 hours. The resin has an acid number of 3 mg KOH/g and an ICI melt viscosity of 15 poise at 200°C. 1,4-Cyclohexanedicarboxylic acid (238.2 g) was added at 230°C and the melt agitated at
35 230°C for 4 hours. The molten resin was poured to a

- 19 -

syrup can where it cooled to a solid with the following properties:

	I.V.	0.174 dl/g
5	ICI Melt Viscosity at 200°C	31 poise
	Acid Number	47
	Hydroxyl Number	5
	DSC (2nd cycle)	
	Tg	60°C
10	Gel permeation chromatography	
	Mw	6,263
	Mn	1,904
15	Carboxyl Resin CC	

This example illustrates the typical procedure for preparing the all-aliphatic semi-crystalline polyester of this invention.

- 20 A 3000 mL, 3-necked, round bottom flask equipped with a stirrer, a short distillation column, and an inlet for nitrogen, was charged with dimethyl cyclohexanedicarboxylate (1280.8 g, 6.40 mol), 1,4-butanediol (692.9g 7.683 mol, 10% excess), and 100 ppm of titanium
- 25 tetraisopropoxide in 2-propanol. The flask and contents were heated under nitrogen atmosphere to a temperature of 170°C at which point methanol begins to distill rapidly from the flask. After the reaction mixture was heated with stirring at this temperature for about 1
- 30 hour, the temperature was increased to 200°C for 2 hours, raised to 215°C for 4 hours, and then to 235°C. After 3 hours at this temperature, a vacuum of 10 mm of mercury was applied over a period of 12 minutes. Stirring was continued under 10 mm of mercury at 235°C
- 35 for about 3 hours to produce a low melt viscosity,

- 20 -

colorless polymer. The resulting polymer was cooled to 200°C and 1,4-cyclohexanedicarboxylic acid (228.7 g, 1.33 mol) was added. Heating with stirring was continued for about 4 hours to produce a resin with an inherent viscosity of 0.21, a melting point of 134°C, an acid number of 47, and a molecular weight by GPC of 2200.

Example Powder 1A - Powder Coating from 70/30 Resin CA/CC and β -hydroxylalkylamide

This example provides a coating with excellent UV resistance and excellent impact resistance.

Carboxyl Resin CA (260 g), Resin CC (112 g), PRIMID XL552 (28.0 g), MODAFLOW 2000 (6.0 g), benzoin (1.0 g), TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium dioxide (200.0 g) were mixed in a Vitamix mixer and compounded in an APV extruder at 130°C. The extrudate was cooled, granulated, and pulverized in a Bantam mill with liquid nitrogen bled into the grinding chamber. The powder was classified through a 200 mesh screen. The powder was electrostatically applied to a 3 in. x 9 in. metal panel and cured in a 350°F oven for 20 minutes. The film properties are as follows:

- 21 -

	Film thickness, Mil	2.2
	Impact strength, (in./lb)	
	Front	160
	Reverse	160
5	Pencil Hardness	F
	Gloss	
	20 deg	57
	60 deg	86
	MEK double rubs	more than 200
10	QUV, hours to 50% loss	>2300 hrs.

15 Example Powder 2A - Powder Coating from 50/50 Resin
 CA/CC and β -hydroxylalkylamide

20 This example provides a coating with excellent UV
resistance and excellent impact.

 Resin CA (186 g), resin CC (186 g), PRIMID XL552
(28.0 g), MODAFLOW 2000 (6.0 g), benzoin (1.0 g),
25 TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium
dioxide (200.0 g) were mixed in a Vitamix mixer and
compounded in an APV extruder at 130°C. The extrudate
was cooled, granulated, and pulverized in a Bantam mill
with liquid nitrogen bled into the grinding chamber.
The powder was classified through a 200 mesh screen.
30 The powder was electrostatically applied to a 3 in. x 9
in. metal panel and cured in a 350°F oven for 20
minutes. The film properties are as follows:

- 22 -

	Film thickness, Mil	2.2
	Impact strength, (in./lb)	
	Front	160
	Reverse	160
5	Pencil Hardness	HB
	Gloss	
	20 deg	47
	60 deg	81
	MEK double rubs	more than 200
10	QUV, hours to 50% loss	1600

Example Powder 3B - Powder Coating from 70/30 Resin
CB/CC and β -hydroxylalkylamide

15

This example provides a coating with excellent UV resistance and excellent impact.

Resin CB (260 g), Resin CC (112 g), PRIMID XL552 (28.0 g), MODAFLOW 2000 (6.0 g), benzoin (1.0 g),
20 TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium dioxide (200.0 g) were mixed in a Vitamix mixer and compounded in an APV extruder at 130°C. The extrudate was cooled, granulated, and pulverized in a Bantam mill with liquid nitrogen bled into the grinding chamber.
25 The powder was classified through a 200 mesh screen. The powder was electrostatically applied to a 3 in. x 9 in. metal panel and cured in a 375°F oven for 20 minutes. The film properties are as follows:

- 23 -

	Film thickness, Mil	2.3
	Impact strength, (in./lb)	
	Front	160
	Reverse	160
5	Pencil Hardness	HB
	Gloss	
	20 deg	62
	60 deg	88
	MEK double rubs	more than 200
10	QUV, hours to 50% loss	>2600

15 Example Powder 4B - Powder Coating from 50/50 Resin
CB/CC and β -hydroxylalkylamide

20 This example provides a coating with excellent UV
resistance and excellent impact.

Resin CB (186 g), Resin CC (186 g), PRIMID XL552 (28.0 g), MODAFLOW 2000 (6.0 g), benzoin (1.0 g),
25 TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium dioxide (200.0 g) were mixed in a Vitamix mixer and compounded in an APV extruder at 130°C. The extrudate was cooled, granulated, and pulverized in a Bantam mill with liquid nitrogen bled into the grinding chamber.
30 The powder was classified through a 200 mesh screen. The powder was electrostatically applied to a 3 in. x 9 in. metal panel and cured in a 350°F oven for 20 minutes. The film properties are as follows:

- 24 -

	Film thickness, Mil	2.0
	Impact strength, (in./lb)	
	Front	160
	Reverse	160
5	Pencil Hardness	2B
	Gloss	
	20 deg	47
	60 deg	83
	MEK double rubs	more than 200
10	QUV, hours to 50% loss	1900

Comparative Example 5A - Powder Coating from Resin CA
and β -hydroxylalkylamide

15

This comparative example provides a coating with excellent UV resistance but poor impact.

20 Resin CA (372 g), PRIMID XL552 (28.0 g), MODAFLOW 2000 (4.0 g), benzoin (1.0 g), TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium dioxide (200.0 g) were mixed in a Vitamix mixer and compounded in an APV extruder at 130°C. The extrudate was cooled, granulated, and pulverized in a Bantam mill with liquid

25 nitrogen bled into the grinding chamber. The powder was classified through a 200 mesh screen. The powder was electrostatically applied to a 3 in. x 9 in. metal panel and cured in a 325°F oven for 20 minutes. The film properties are as follows:

30

- 25 -

	Film thickness, Mil	2.2
	Impact strength, (in./lb)	
	Front	40
	Reverse	20
5	Pencil Hardness	H
	Gloss	
	20 deg	68
	60 deg	89
	MEK double rubs	200
10	QUV, hours to 50% loss	2200

Comparative Example 6B - Powder Coating from Resin CB
and β -hydroxylalkylamide

15

This comparative example provides a coating with excellent UV resistance but poor impact (40/20 front/reverse).

20

Carboxyl Resin CB (372 g), PRIMID XL552 (28.0 g), MODAFLOW III (6.0 g), benzoin (1.0 g), TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium dioxide (200.0 g) were mixed in a Vitamix mixer and compounded in an APV extruder at 130°C. The extrudate was cooled,

25

granulated, and pulverized in a Bantam mill with liquid nitrogen bled into the grinding chamber. The powder was classified through a 200 mesh screen. The powder was electrostatically applied to a 3 in. x 9 in. metal panel and cured in a 375°F oven for 20 minutes. The film

30

properties are as follows:

- 26 -

	Film thickness, Mil	2.0
	Impact strength, (in./lb)	
	Front	40
	Reverse	20
5	Pencil Hardness	F
	Gloss	
	20 deg	72
	60 deg	88
	MEK double rubs	200
10	QUV, hours to 50% loss	>1600
15	Comparative Example 7 - Powder Coating from Commercial Rucote 915 and β -hydroxyl- alkylamide	

- 20 This comparative example shows that aromatic resin has fair impact but poor UV resistance.
- 25 Carboxyl resin RUCOTE 915 (379.0 g), PRIMID XL552 (21.0 g), MODAFLOW III (4.0 g), benzoin (1.0 g), TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium dioxide (200.0 g) were mixed in a Vitamix mixer and compounded in an APV extruder at 130°C. The extrudate was cooled, granulated, and pulverized in a Bantam mill with liquid nitrogen bled into the grinding chamber. The powder was
- 30 classified through a 200 mesh screen. The powder was electrostatically applied to a 3 in. x 9 in. metal panel and cured in a 325°F oven for 20 minutes. The film properties are as follows:

- 27 -

	Film thickness, Mil	2.0
	Impact strength, (in./lb)	
	Front	40
	Reverse	80
5	Pencil Hardness	F
	Gloss	
	20 deg	78
	60 deg	95
	MEK double rubs	200
10	QUV, hours to 50% loss	230

Comparative Example 8 - Powder Coating from Commercial
Resin EMS GRILESTA 7612 and
 β -hydroxyalkylamide

15

This comparative example shows that aromatic resin
has good impact but poor UV resistance.

20

Carboxyl resin EMS GILESTA 7612 (379.0 g), PRIMID
XL552 (21.0 g), MODAFLOW III (4.0 g), benzoin (1.0 g),
TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium
dioxide (200.0 g) were mixed in a Vitamix mixer and
compounded in an APV extruder at 130°C. The extrudate
was cooled, granulated, and pulverized in a Bantam mill
with liquid nitrogen bled into the grinding chamber. The
powder was classified through a 200 mesh screen. The
powder was electrostatically applied to a 3 in. x 9 in.
metal panel and cured in a 350°F oven for 20 minutes.

25

30

The film properties are as follows:

- 28 -

	Film thickness, Mil	21.1
	Impact strength, (in./lb)	
	Front	160
	Reverse	160
5	Pencil Hardness	H
	Gloss	
	20 deg	73
	60 deg	92
	MEK double rubs	200
10	QUV, hours to 50% loss	250

Comparative Example 9 - Powder Coatings from Carboxyl
Resin EMS GRILESTA 7309 and TGIC

15

This example shows aromatic resin with TGIC has good impact but poor UV resistance.

20 Carboxyl EMS GILESTA 7309 (372.0 g), Triglycidyl-
isocyanurate (TGIC) (28.0 g), MODAFLOW III (4.0 g),
benzoin (1.0 g), TINUVIN 144 (5.6 g), TINUVIN 234
(5.6 g), and titanium dioxide (160.0 g) were mixed in a
Vitamix mixer and compounded in an APV extruder at
25 130°C. The extrudate was cooled, granulated, and
pulverized in a Bantam mill with liquid nitrogen bled
into the grinding chamber. The powder was classified
through a 200 mesh screen. The powder was electro-
statically applied to a 3 in. x 9 in. metal panel and
cured in a 350°F oven for 20 minutes. The film
30 properties are as follows:

- 29 -

	Film thickness, Mil	1.9
	Impact strength, (in./lb)	
	Front	160
	Reverse	160
5	Pencil Hardness	H
	Gloss	
	20 deg	63
	60 deg	82
	MEK double rubs	200
10	QUV, hours to 50% loss	250

Hydroxyl Resins

15 Hydroxyl Resin HA

20 To a 1000 ml, 3-neck round bottom flask were added
2,2,4,4-tetramethyl-1,3-cyclobutanediol (209.0 g, 1.450
moles), 2,2-dimethyl-1,3-propanediol (36.1 g, 0.347
moles), trimethylolpropane (18.1 g, 0.135 moles) and
FASCAT 4100 (0.5 g). The contents were heated to melt
at 180°C and 1,4-cyclohexanedicarboxylic acid (306.5 g,
1.780 moles) is added. The flask was swept with 1.0
25 scfh nitrogen while the temperatures was raised from
180°C to 230°C over a 6-hour period. The batch
temperature was maintained at 230°C for 8 hours. The
molten resin was poured to a syrup can where it cooled
to a solid with the following properties:

30

- 30 -

	I.V.	0.249
	ICI Melt Viscosity at 200°C	poise
	Acid Number	2.6
	Hydroxyl Number	28.0
5	DSC (2nd cycle)	
	Tg	49°C
	Gel permeation chromatography	
	Mw	19,841
	Mn	4,750

10

Hydroxyl Resin HB

- 15 To a 1000 ml, 3-neck round bottom flask were added 2,2,4,4-tetramethyl-1,3-cyclobutanediol (209.0 g, 1.450 moles), 2,2-dimethyl-1,3-propanediol (40.2 g, 0.387 moles), trimethylolpropane (12.7 g, 0.095 moles) and Fascat 4100 (0.5 g). The content was heated to melt at
- 20 180°C and 1,4-cyclohexanedicarboxylic acid (307.2 g, 1.784 moles) was added. The flask was swept with 1.0 scfh nitrogen while the temperatures was raised from 180°C to 230°C over a 6-hour period. The batch temperature was maintained at 230°C for 8 hours. The
- 25 molten resin was poured to a syrup can where it cooled to a solid with the following properties:

- 31 -

	I.V.	0.233
	ICI Melt Viscosity at 200°C	poise
	Acid Number	3.4
	Hydroxyl Number	42.4
5	DSC (2nd cycle)	
	Tg	47°C
	Gel permeation chromatography	
	Mw	16,233
	Mn	3,806

10

Hydroxyl Resin HC

This example illustrates the typical procedure for preparing the aliphatic semi-crystalline polyesters of this invention which are in this example, hydroxyl-functional. A 3000 mL, 3-necked, round-bottom flask equipped with a stirrer, a short distillation column, and an inlet for nitrogen, was charged with dimethyl cyclohexanedicarboxylate (1259.7 g, 6.29 mol), 1,4-butanediol (997.5 g, 11.08 mol), trimethylolpropane (73.9 g, 0.55 moles) and 10 mL of titanium tetraisopropoxide/2-propanol solution (100 ppm Ti). The flask and contents were heated under nitrogen atmosphere to a temperature of 170°C at which point methanol began to distill rapidly from the flask. After the reaction mixture was heated with stirring at this temperature for about 1 hour, the temperature was increased to 200°C for 2 hours, raised to 215°C for 4 hours, and then to 235°C. After 3 hours at this temperature, a vacuum of 10 mm of mercury was applied over a period of 18 minutes. Stirring was continued under 10 mm of mercury at 235°C for about 3 hours to produce a low melt viscosity, colorless polymer. The polymer has an inherent viscosity of 0.30, a melting point of 130°C, and a hydroxyl number of 30.

- 32 -

Example Powder 10A - Powder Coating from 50/50 Resin
HA/HC and ϵ -caprolactam Blocked
Isophoronediiisocyanate

5

This example provides a coating with excellent UV resistance and excellent impact.

Resin HA (160 g), Resin HC (160 g), Huls BF 1540 (80.0 g), benzoin (6.0 g), MODAFLOW 2000 (6.0 g),
10 TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium dioxide (160.0 g) were mixed in Vitamix mixer and compounded in an APV extruder at 125°C. The extrudate was cooled, granulated, and pulverized in a Bantam mill with liquid nitrogen bled into the grinding chamber.
15 The powder was classified through a 200 mesh screen. The powder was electrostatically applied to a 3 in. x 9 in. metal panel and cured in a 350°F oven for 20 minutes. The film properties are as follows:

20	Film thickness, Mil	1.8
	Impact strength, (in./lb)	
	Front	160
	Reverse	160
	Pencil Hardness	B
25	Gloss	
	20 deg	67
	60 deg	92
	MEK double rubs	more than 200
	QUV, hours to 50% loss	>2300

30

Example Powder 11A - Powder Coating from 50/50 Resin
HA/HC and Self-blocked
Isophoronediiisocyanate

35

This example provides a coating with excellent UV resistance and excellent impact.

Resin HA (160 g), Resin HC (160 g), Huls BF 1540

- 33 -

(80.0 g), benzoin (6.0 g), MODAFLOW 2000 (6.0 g),
TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium
dioxide (160.0 g) were mixed in Vitamix mixer and
compounded in an APV extruder at 125°C. The extrudate
5 was cooled, granulated, and pulverized in a Bantam mill
with liquid nitrogen bled into the grinding chamber.
The powder was classified through a 200 mesh screen.
The powder was electrostatically applied to a 3 in. x 9
in. metal panel and cured in a 375°F oven for 20
10 minutes. The film properties are as follows:

	Film thickness, Mil	1.8
	Impact strength, (in./lb)	
	Front	160
15	Reverse	160
	Pencil Hardness	B
	Gloss	
	20 deg	63
	60 deg	89
20	MEK double rubs	more than 200
	QUV, hours to 50% loss	>1500

25 Example Powder 12A - Powder Coating from 50/50 Resin
HB/HC and POWDERLINK 1174
Crosslinker

30 Resin HB (188 g), Resin HC (188 g), POWDERLINK 1174
(24.0 g), methyl tolyl sulfonimide (5.0 g), benzoin (6.0
g), MODAFLOW 2000 (6.0 g), TINUVIN 144 (6.0 g), TINUVIN
35 234 (6.0 g), and titanium dioxide (160.0 g) were mixed
in Vitamix mixer and compounded in an APV extruder at
125°C. The extrudate was cooled, granulated, and
pulverized in a Bantam mill with liquid nitrogen bled

- 34 -

into the grinding chamber. The powder was classified through a 200 mesh screen. The powder was electrostatically applied to a 3 in. x 9 in. metal panel and cured in a 350°F oven for 20 minutes. The film

5 properties are as follows:

	Film thickness, Mil	1.9
	Impact strength, (in./lb)	
	Front	160
10	Reverse	160
	Pencil Hardness	2B
	Gloss	
	20 deg	40
	60 deg	85
15	MEK double rubs	more than 200
	QUV, hours to 50% loss	>1500

20 Comparative 13A - Powder Coatings from Resin HA and
Caprolactam Blocked
Isophoronediiisocyanate

25 This comparative shows that Resin HA produces
coating with excellent QUV but poor impact.

Resin HA (415 g), Huls 1530 (99.4 g), dibutyltin dilaurate (5.1 g), benzoin (5.1 g), MODAFLOW III (7.7 g), TINUVIN 144 (5.1 g), TINUVIN 234 (5.1 g), and titanium dioxide (205.7 g) were mixed in a Vitamix mixer and compounded in an APV extruder at 120°C. The extrudate was cooled, granulated, and pulverized in a Bantam mill with liquid nitrogen bled into the grinding chamber. The powder was classified through a 200 mesh screen. The powder was electrostatically applied to a 3 in. x 9 in. metal panel and cured in a 400°F oven for 10 minutes. The film properties are as follows:

- 35 -

	Film thickness, Mil	1.5
	Impact strength, (in./lb)	
	Front	40
	Reverse	20
5	Pencil Hardness	F
	Gloss	
	20 deg	67
	60 deg	85
	MEK double rubs	200
10	QUV, hours to 50% loss of gloss	2100

Comparative 14B - Powder Coatings from Resin HB and
POWDERLINK 1174 Crosslinker

15

This comparative shows that HB produces coating with excellent QUV but poor impact.

20 Resin HB (376 g), POWDERLINK 1174 (24.0 g), methyl tolyl sulfonimide (5.0 g), benzoin (4.0 g), MODAFLOW 2000 (6.0 g), TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and titanium dioxide (160.0 g) were mixed in Vitamix mixer and compounded in an APV extruder at 125°C. The extrudate was cooled, granulated, and pulverized in a
25 Bantam mill with liquid nitrogen bled into the grinding chamber. The powder was classified through a 200 mesh screen. The powder was electrostatically applied to a 3 in. x 9 in. metal panel and cured in a 350°F oven for 20 minutes. The film properties are as follows:

30

- 36 -

	Film thickness, Mil	1.8
	Impact strength, (in./lb)	
	Front	20
	Reverse	<20
5	Pencil Hardness	H
	Gloss	
	20 deg	73
	60 deg	93
	MEK double rubs	200
10	QUV, hours to 50% loss of gloss	>1500

Comparative Example 15 - Powder Coatings from Hydroxyl
RUCOTE 107 and ϵ -Caprolactam
Blocked Isophoronediiisocyanate

15 This comparative shows commercial aromatic resin produces coating with good impact but poor QUV.

20 RUCOTE 107 (800 g), Huls 1530 (200.0 g), benzoin (10.0 g), MODAFLOW III (10.0 g), TINUVIN 144 (14.3 g), TINUVIN 234 (14.3 g), and titanium dioxide (400.0 g) were mixed in a Henschel mixer and compounded in an ZSK 30 extruder. The extruder temperature profile was Feed

25 zone = 110°C, die zone = 125°C, and a screw speed of 250 rpm with feeding rate enough to maintain 45% torque. The extrudate was cooled through a chill roll, granulated and pulverized using a Bantam mill with liquid nitrogen bled into the grinding chamber. The

30 powder was classified through a 200 mesh screen, electrostatically applied to 3 in. x 9 in. metal panels and cured in a 350°F oven for 20 minutes. The film properties are as follows:

- 37 -

	Film thickness, Mil	2.0
	Impact strength, (in./lb)	
	Front	160
	Reverse	160
5	Pencil Hardness	H
	Gloss	
	20 deg	84
	60 deg	95
	MEK double rubs	200
10	QUV, hours to 50% loss of gloss	240

Examples 16-26

15 Carboxyl Resin I

20 To a 3000 ml, 3-neck round bottom flask were added hydrogenated bisphenol A (726.5 g, 3.027 moles), 2,2-dimethyl-1,3-propanediol (326.4 g, 2.847 moles) and trimethylolpropane (24.3 g, 0.183 moles) and FASCAT 4100 (1.8 g). The contents were heated to melt at 180°C.

25 1,4-Cyclohexanedicarboxylic acid (951.7 g, 5.526 moles) was added. The flask was swept with 1.0 scfh nitrogen while the temperature was raised from 180°C to 230°C over a 6-hour period. The batch temperature was

30 maintained at 230°C for 8 hours. The resulting resin has an acid number of 3 mg KOH/g and an ICI melt viscosity of 15 poise at 200°C. 1,4-Cyclohexane-dicarboxylic acid (238.2 g) was added at 230°C and the melt was agitated at 230°C for 4 hours. The molten resin was poured into a syrup can where it cooled to a solid with the following properties:

- 38 -

	I.V.	0.174 dl/g
	ICI Melt Viscosity at 200°C	31 poise
	Acid Number	47
	Hydroxyl number	5
5	DSC (2nd cycle)	
	Tg	60°C
	Gel permeation chromatography	
	Mw	6,263
	Mn	1,904

10

Carboxyl Resin II

A 3000 mL, 3-necked, round bottom flask equipped with a stirrer, a short distillation column, and an inlet for nitrogen, was charged with dimethyl
15 cyclohexanedicarboxylate (1280.8 g, 6.40 mol), 1,4-butanediol (692.9 g, 7.683 mol, 10% excess), and 100 ppm of titanium tetraisopropoxide in 2-propanol. The flask and contents were heated under nitrogen atmosphere to a temperature of 170°C at which point methanol began to
20 distill rapidly from the flask. After the reaction mixture was heated with stirring at this temperature for about 1 hour, the temperature was increased to 200°C for 2 hours, raised to 215°C for 4 hours, and then to 235°C. After 3 hours at this temperature, a vacuum of 10 mm of
25 mercury was applied over a period of 12 minutes. Stirring was continued under 10 mm of mercury at 235°C for about 3 hours to produce a low melt viscosity, colorless polymer. The resulting polymer was cooled to 200°C and 1,4-cyclohexanedicarboxylic acid (228.7 g,
30 1.33 mol) was added. Heating with stirring was continued for about 4 hours to produce a resin with an inherent viscosity of 0.21, a melting point of 134°C, an acid number of 47, and a molecular weight by GPC of 2200.

35

- 39 -

Powder coating composition Examples 16 through 22.
Powder coatings from 50/50 Resin I/II and
 β -hydroxylalkylamide.

- 5 Resin I (186 g), Resin II (186 g), PRIMID XL552
(28.0 g), MODAFLOW 2000 flow aid (6.0 g), benzoin (1.0
g), TINUVIN 144 (6.0 g), TINUVIN 234 (6.0 g), and
titanium dioxide (200.0 g) were mixed in a Vitamix mixer
and compounded in an APV extruder at 130°C. The
10 extrudate was cooled, granulated, and pulverized in a
Bantam mill with liquid nitrogen bled into the grinding
chamber. The powder was classified through a 200 mesh
screen. The powder coating described above was mixed
with specified amount of catalyst in a Micromill for
15 about 1 minute and the gel time of the resulting powder
was determined. The table below demonstrates that gel
time changes with variety and amount of catalyst.

- 40 -

POWDER #	CATALYST	WT% CONCENTRATION	GEL TIME SECONDS
16	None (control)	0	235
17	Zinc Acetate	1.0	147
18	Zinc Acetate	2.0	137
19	Zinc Stearate	1.0	189
20	Zinc Stearate	3.6	156
21	Titanium Isopropoxide	1.0 Ti	128
22	Zinc Oxide	1.0	163

10

Thermosetting powder coating composition Examples
23 through 26. Powder coatings from 50/50 Resin
I/II, β -hydroxylalkylamide and zinc stearate
coextruded.

15

Resin I (372 g), Resin II (372 g), PRIMID XL552
(56.0 g), zinc stearate (amount specified in table
below), MODAFLOW 2000 (12.0 g), benzoin (2.0 g), TINUVIN
144 (12.0 g), TINUVIN 234 (12.0 g), and titanium dioxide
(400.0 g) were mixed in a Henschel mixer and compounded
in an ZSK 30 extruder. The extruder temperature profile
was Feed zone = 110°C, die zone = 110°C, and a screw
speed of 400 rpm. The extrudate was cooled through a
chill roll, granulated and pulverized using a Bantam
mill with liquid nitrogen bled into the grinding
chamber. The powder was classified through a 200 mesh

20
25

- 41 -

screen. Gel time taken from these powders are listed below.

5	POWDER #	CATALYST	GRAM	GEL TIME SECONDS
	23	None (control)	0	245
	24	Zinc Acetate	12.0	188
	25	Zinc Stearate	12.0	197
	26	Zinc Stearate	43.0	169

10

- 42 -

CLAIMS

We claim:

- 5 1. A thermosetting coating composition comprising
- (a) an amorphous polyester comprised of residues
 of cyclohexanedicarboxylic acid and a cyclo-
 aliphatic diol, said amorphous polyester
10 having a glass transition temperature (T_g) of
 about 50°C to 70°C and a hydroxyl or an acid
 number of about 30 to 80;
- (b) a semicrystalline polyester comprised of
15 residues of cyclohexanedicarboxylic acid and a
 linear diol, said linear diol having 4, 6, 8
 or 10 carbon atoms, said semicrystalline
 polyester having a T_m of about 60-160°C and a
 hydroxyl or an acid number of about 30-80; and
20
- (c) a cross-linking effective amount of a cross-
 linking agent.
- 25 2. A thermosetting coating composition comprising
- (a) an amorphous polyester comprised of residues
 of cyclohexanedicarboxylic acid and a cyclo-
 aliphatic diol, said amorphous polyester
 having a glass transition temperature (T_g) of
30 about 50°C to 70°C and a hydroxyl or an acid
 number of about 30 to 80;
- (b) a semicrystalline polyester comprised of
 residues of cyclohexanedicarboxylic acid and a
35 linear diol, said linear diol having 4, 6, 8

- 43 -

- or 10 carbon atoms, said semicrystalline polyester having a T_m of about 60–160°C and a hydroxyl or an acid number of about 30–80; provided that when (a) has an acid number of 30 to 80, (b) has an acid number of 30 to 80, and when (a) has a hydroxyl number of 30 to 80, (b) has a hydroxyl number of 30 to 80; and
- (c) a cross-linking effective amount of a cross-linking agent.
3. The composition of claim 1, wherein the cycloaliphatic diol is selected from the group consisting of hydrogenated bisphenol A; 2,2,4,4-tetramethyl-1,3-cyclobutanediol; tricyclodecane dimethanol; and 1,4-cyclohexanediol.
4. The composition of claim 2, wherein the cycloaliphatic diol is selected from the group consisting of 2,2,4,4-tetramethyl-1,3-cyclobutanediol; hydrogenated bisphenol A; and 1,4-cyclohexanediol.
5. The composition of claim 1 or 2, wherein component (b) is further comprised of about 1 to about 12 weight percent of residues of trimethylolpropane, based on the weight of component (b).
6. The composition of claim 2, wherein component (a) has a hydroxyl number of about 30 to 80; component (b) has a hydroxyl number of about 30 to 80; and component (c) is a blocked isocyanate, a glycoluril, or a melamine type crosslinker.
7. The composition of claim 2 or 6, wherein the

- 44 -

5 blocked isocyanate is selected from the group consisting of ϵ -caprolactam-blocked isophoronediiisocyanate; ϵ -caprolactam-blocked toluene 2,4-diisocyanate; and the self-blocked uretidione of isophoronediiisocyanate.

8. The composition of claim 2, wherein component (a) has an acid number of about 30 to 80; component (b) has an acid number of about 30 to 80; and component
10 (c) is an epoxy compound or resin or a β -hydroxyl-alkyl amide.
9. The composition of claim 2 or 8, wherein component
15 (c) is triglycidylisocyanurate or Bis(N,N-dihydroxyethyl)adipamide.
10. A shaped or formed article coated with the cured composition of claim 1.
- 20 11. A shaped or formed article coated with the cured composition of claim 2.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 94/06564

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09D167/02 C08G18/42 C09D175/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09D C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,91 14745 (COURTAULDS COATINGS LTD) 3 October 1991 see claims 1-29 ---	1-5,8-11
A	WO,A,92 14770 (EASTMAN KODAK COMPANY) 3 September 1992 see claims 1-24 ---	1-11
A	EP,A,0 408 465 (EASTMAN KODAK COMPANY) 16 January 1991 see claims 1-23 -----	1-11

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "I" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

20 October 1994

Date of mailing of the international search report

- 8. 11. 94

Name and mailing address of the ISA

European Patent Office, P.B. 2818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+ 31-70) 340 2040, Tx. 31 651 epo nl,
 Fax (+ 31-70) 340-3016

Authorized officer

Decocker, L

INTERNATIONAL SEARCH REPORT

Information from patent family members

International Application No.

PCT/US 94/06564

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9114745	03-10-91	AU-A- 7559791 EP-A- 0521992 GB-A, B 2244060	21-10-91 13-01-93 20-11-91
WO-A-9214770	03-09-92	CA-A- 2103709 EP-A- 0572520 JP-T- 6505297	20-08-92 08-12-93 16-06-94
EP-A-0408465	16-01-91	CA-A- 2058760 DE-D- 69006953 DE-T- 69006953 EP-A- 0479851 JP-T- 4505939 WO-A- 9100306	27-12-90 07-04-94 22-09-94 15-04-92 15-10-92 10-01-91